

Rate Law and the Eyring Equation

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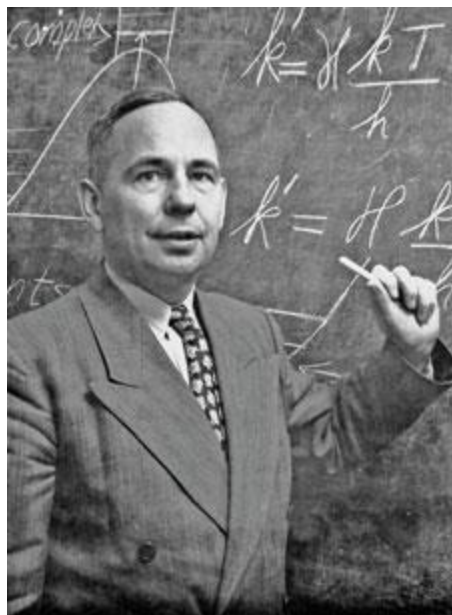
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Abstract

When we talk about the rate of a chemical reaction, what we mean is the rate at which reactants are converted into products. The rate of a reaction decreases as time progresses. In this article, we provide insight into the derivation of the rate of decrease of reaction velocity with time and **Eyring Equation** which can be applied with considerable success to a wide variety of rate processes.



Henry Eyring was a Mexico-born United States theoretical chemist whose primary contribution was in the study of chemical reaction rates and intermediates.

The dependence of the reaction rate on the concentrations of reacting substances is given by the **Law of Mass Action**. This law states that the rate of a chemical reaction is directly proportional to the product of the molar concentrations of the reactants at any constant temperature at any given time. For a general reaction,



The rate law can be written as:

$$v = - \frac{dC}{dt} = kC^n$$

where C express the concentration of the reactant "A", k the reaction rate constant or rate coefficient of the reaction and n the order of the reaction. As we increase the temperature the rate of reaction "v" increases. As a rough approximation, for many reactions happening at around

room temperature, the **rate of reaction** doubles for every 10°C rise in temperature. Differentiating this expression with respect to temperature, we obtain:

$$\frac{dv}{dT} = \frac{dk}{dT} C^n + \frac{dC^n}{dT} k$$

$$\frac{dv}{dT} = \frac{dk}{dT} C^n + nC^{n-1} \frac{dC}{dT} k$$

Since $d \ln k = \frac{dk}{k}$. Therefore:

$$\frac{dv}{dT} = \frac{d \ln k}{dT} k C^n + nC^{n-1} \frac{dC}{dT} k$$

Each reaction rate coefficient k has a temperature dependency, which is usually given by the equation:

$$\frac{d \ln k}{dT} = \frac{E_a}{RT^2}$$

where E_a is the activation energy and R is the gas constant.

$$\frac{dv}{dT} = \frac{E_a}{RT^2} v + \frac{nv}{C} \frac{dC}{dT}$$

$$\frac{dv}{dt} = \frac{dT}{dt} \frac{E_a}{RT^2} v + \frac{nv}{C} \frac{dC}{dt}$$

Heat capacity or thermal capacity is a physical property of matter, defined as the amount of heat to be supplied to a given mass of a material to produce a unit change in its temperature. The heat capacity of an object, denoted by c , is given by the equation:

$$c = \frac{dQ}{dT}$$

$$\frac{dv}{dt} = \frac{dQ}{dt} \frac{E_a}{cRT^2} v + \frac{nv}{C} \frac{dC}{dt}$$

During the course of the reaction, reactant **A** is consumed to form products. Physically, it reminds us that the concentration of the reactant **A** decreases with time – which leads to a decreased reaction rate as time progresses.

$$-\frac{dv}{dt} = \left(-\frac{dQ}{dt}\right) \frac{E_a}{cRT^2} v + \frac{nv}{C} \left(-\frac{dC}{dt}\right)$$

$$-\frac{dv}{dt} = v_{\text{rate}} \frac{E_a}{cRT^2} v + \frac{nv}{C} v$$

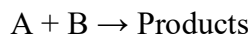
where v_{rate} is the rate of absorption of heat energy.

$$-\frac{dv}{dt} = v_{\text{rate}} \frac{E_a}{cRT^2} v + \frac{nv^2}{C}$$

Eyring Equation:

The Eyring Equation gives a more accurate calculation of rate constants and provides insight into how a reaction progresses at the molecular level.

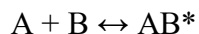
Consider a bimolecular reaction:



In the transition state model, the activated complex AB* is formed:



For a reaction:



The change in free energy is given by the equation:

$$\Delta G = \Delta G^0 + RT \ln Q$$

where R is the gas constant ($8.314 \frac{\text{J}}{\text{Kmol}}$), T is the temperature in Kelvin scale, ln represents logarithm to the base e, ΔG^0 is the Gibbs free energy change when all the reactants and products are in their standard state and Q is the reaction quotient or reaction function at any given time ($Q = \frac{[AB^*]}{[A][B]}$). We may resort to thermodynamics and write for ΔG^0 :

$$\Delta G^0 = - RT \ln K_{eq}$$

where K_{eq} is the equilibrium constant for the reaction. If K_{eq} is greater than 1, $\ln K_{eq}$ is positive, ΔG^0 is negative; so the forward reaction is favored. If K_{eq} is less than 1, $\ln K_{eq}$ is negative, ΔG^0 is positive; so the backward reaction is favored. It can be shown that:

$$\Delta G = - RT \ln K_{eq} + RT \ln Q$$

The rate of formation of activated complex is given by:

$$v_1 = k_1 [A] [B]$$

where k_1 is the rate constant of the forward reaction. The rate of dissociation of the activated complex to give back the reactants is given by:

$$v_2 = k_2 [AB^*]$$

where k_2 is the rate constant of the backward reaction. Further, the ratio $\frac{v_1}{v_2}$ yields:

$$\frac{v_1}{v_2} = \frac{k_1}{Q k_2}$$

But

"Equilibrium constant is the ratio of the rate constant of the forward reaction to the rate constant of the backward reaction"

and, consequently,

$$\frac{v_1}{v_2} = \frac{K_{eq}}{Q}$$

At equilibrium $v_1 = v_2$, hence $Q = K_{eq}$. On taking natural logarithms of the above equation we get:

$$\ln \left(\frac{v_1}{v_2} \right) = \ln K_{eq} - \ln Q$$

On multiplying by $-RT$ on both sides, we obtain,

$$-RT \ln \left(\frac{v_1}{v_2} \right) = -RT \ln K_{eq} + RT \ln Q$$

Comparing Equations:

$$\Delta G = -RT \ln K_{eq} + RT \ln Q$$

and $-RT \ln \left(\frac{v_1}{v_2}\right) = -RT \ln K_{eq} + RT \ln Q$, the Gibbs free energy change is seen to be:

$$\Delta G = -RT \ln \left(\frac{v_1}{v_2}\right)$$

If the forward reaction is favored, $\frac{v_1}{v_2}$ is greater than 1, $\ln \left(\frac{v_1}{v_2}\right)$ is positive; so the ΔG is negative.

If the backward reaction is favored, $\frac{v_1}{v_2}$ is less than 1, $\ln \left(\frac{v_1}{v_2}\right)$ is negative; so the ΔG is positive.

At equilibrium $v_1 = v_2$, hence

$$\Delta G = 0$$

$$\Delta H = T\Delta S$$

$$T = \frac{\Delta H}{\Delta S}$$

$$Q = e^{-\frac{\Delta G^0}{RT}} e^{\frac{\Delta G}{RT}}$$

$$\frac{[AB^*]}{[A][B]} = e^{-\frac{\Delta G^0}{RT}} \frac{v_2}{v_1}$$

The rate of reaction is given by:

$$v = k [A] [B] = \kappa \frac{k_B T}{h} [AB^*]$$

where κ is the transmission coefficient (fraction of $[AB^*]$ crossing forward to products), k_B is Boltzmann's constant, and h is Planck's constant.

$$\frac{v_1}{v_2} = e^{-\frac{\Delta G^0}{RT}} \frac{\kappa \frac{k_B T}{h}}{k}$$

$$k = \kappa \frac{k_B T}{h} \frac{v_2}{v_1} e^{-\frac{\Delta G^0}{RT}}$$



Svante August Arrhenius was a Swedish scientist. Originally a physicist, but often referred to as a chemist, Arrhenius was one of the founders of the science of physical chemistry. He received the Nobel Prize for Chemistry in 1903, becoming the first Swedish Nobel laureate.

For correct dimensionality, the equation needs to have an extra factor of $(c^\ominus)^{1-m}$ for reactions that are not unimolecular:

$$k = \kappa \frac{k_B T}{h} \frac{v_2}{v_1} e^{-\frac{\Delta G^0}{RT}} (c^\ominus)^{1-m}$$

where c^\ominus is the standard concentration 1 mol / L and m is the molecularity.

The rate constant for a bimolecular reaction, as predicted by Arrhenius Equation is:

$$k = A e^{-\frac{E_a}{RT}}$$

E_a is the energy of activation of the reaction and A is Arrhenius frequency factor.

$$A e^{-\frac{E_a}{RT}} = \kappa \frac{k_B T}{h} \frac{v_2}{v_1} e^{-\frac{\Delta H^0}{RT}} e^{\frac{\Delta S^0}{R}}$$

Although the standard enthalpy of activation, ΔH^0 , is often equated with Arrhenius's activation energy E_a , they are not equivalent. For a condensed-phase (e.g., solution-phase) or unimolecular gas-phase reaction step, $E_a = \Delta H^0 + RT$.

$$A = \kappa \frac{k_B T}{h} \frac{v_2}{v_1} e^{(1 + \frac{\Delta S^0}{R})}$$

For other gas-phase reactions, $E_a = \Delta H^0 + (1 - \Delta n) RT$, where Δn is the change in the number of molecules on forming the transition state. (Thus, for a bimolecular gas-phase process, $E_a = \Delta H^0 + 2RT$.)

$$A = \kappa \frac{k_B T}{h} \frac{v_2}{v_1} e^{(2 + \frac{\Delta S^0}{R})}$$

At equilibrium:

$$v_1 = v_2$$

$$\Delta G = 0$$

$$T = \frac{\Delta H}{\Delta S}$$

$$\Delta G^0 = \Delta H^0 - T \Delta S^0$$

$$\Delta G^0 = \Delta H^0 - \frac{\Delta H}{\Delta S} \Delta S^0$$

$$\alpha_1 = \frac{\Delta S^0}{\Delta S}, \alpha_2 = \frac{\Delta H^0}{\Delta H}$$

$$\Delta G^0 = \Delta H (\alpha_2 - \alpha_1)$$

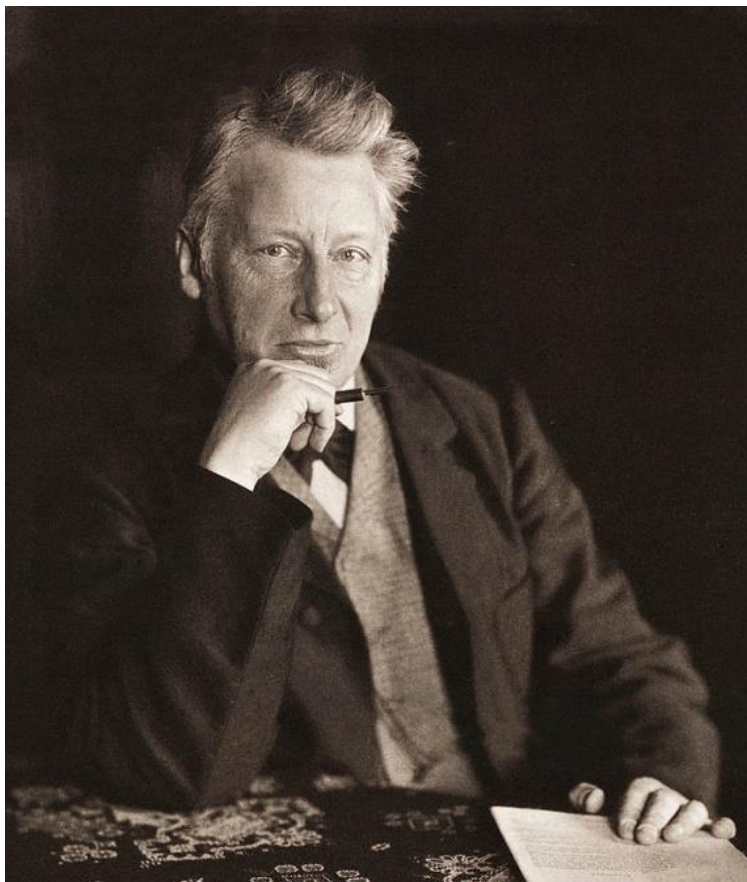
$$k = \kappa \frac{k_B T}{h} \exp \left(- \frac{\Delta H (\alpha_2 - \alpha_1)}{RT} \right) (c^\ominus)^{1-m}$$

$$v = - \frac{dC}{dt} = k C^n$$

$$\frac{dv}{dt} = k \frac{dC^n}{dt} = k n C^{n-1} \times \frac{dC}{dt}$$

$$- \frac{dv}{dt} = k n C^{n-1} \times - \frac{dC}{dt} = \frac{nv^2}{C}$$

$$- \frac{dv}{dt} = \frac{nv^2}{C}$$



Jacobus Henricus van't Hoff was a Dutch physical chemist and first winner of the Nobel Prize for Chemistry (1901), for work on rates of chemical reaction, chemical equilibrium, and osmotic pressure.

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